Structopendant Unsaturated Cellulose Esters via Acylation in Homogeneous Lithium Chloride/*N,N*-Dimethylacetamide Solutions

ZHENG B. ZHANG, CHARLES L. MCCORMICK

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

Received 6 September 1996; accepted 26 March 1997

ABSTRACT: Novel acylation reactions of cellulose were accomplished with a series of unsaturated carboxylic acids or their respective anhydrides including crotonic acid (CRA), methacrylic acid (MAA), vinyl acetic acid (VAA), fumaric acid monoethyl ester (FAME), and cinnamic acid (CINA) in lithium chloride (LiCl)/dimethylacetamide (DMAc) homogeneous solutions. The acylation reactions were conducted at room temperature using dicyclohexylcarbodiimide (DCC) as a condensation agent and 4-dialkylaminopyridine (4-[*N,N*-dimethylamino-] or 4-pyrrolidino-pyridine, DMAP or PP) as a catalyst. A reaction mechanism is proposed based on experimental evidence. The acylated cellulose derivatives obtained from CRA, MAA, or their anhydrides exhibit poor solubility in organic solvents. Side reactions, e.g., the Michael addition, likely occur at the high temperatures required for reaction of these acyl groups. However, acylation of cellulose with VAA, FAME, and CINA is facile with derivatives readily soluble in DMSO. The structures of these derivatized celluloses were characterized with FTIR and ^{1}H-NMR spectroscopy and degrees of substitution were calculated. J Appl Polym Sci **66:** 293–305, 1997

INTRODUCTION

Cellulose, a poly(1 → 4, β-D-anhydroglucose), is the most abundant naturally occurring polysaccharide and has, therefore, been targeted for an enormous number of chemical transformations of commercial utility. The native polysaccharide structure is hydrophilic, rigid, highly functional, and readily biodegradable. Cellulose is usually derivatized to the corresponding ester, ether, or carbamate by reacting the hydroxyl groups on the anhydroglucose rings under heterogeneous reaction conditions. In such reactions, cellulose typically remains suspended in solution and the reaction proceeds from the surface to the amorphous regions. After sufficient reaction or substitution, the crystalline portions gradually become exposed for reaction. Heterogeneous reactions at low degree of substitution (DS) lead to compositional and structural inhomogeneities, including poor uniformity along the cellulosic backbone and extensive byproduct formation. Cellulose derivatives with high DS values normally exhibit improved solubility in solvents and thermal processibility. However, some desirable properties, such as hydrophilicity, moisture uptake, and even biodegradability, are compromised in the high DS derivatives.

More uniform substitution of cellulose derivatives with a controllable DS can be achieved through reactions in a homogeneous solution.[1,2]

Correspondence to: C. L. McCormick.

Contract grant sponsors: Office of Navy Research; Gillette Research Institute; Nalco Corp.

Journal of Applied Polymer Science, Vol. 66, 293–305 (1997)
 CCC 0021-8995/97/020293-13

A number of complexing solvent systems have been investigated including metal/amine, NH_3/NH_4SCN, amine oxides, N_2H_4/DMF, and DMSO/paraformaldehyde.[3,4] In 1979, the dissolution of cellulose in lithium chloride (LiCl) and *N,N*-dimethylacetamide (DMAc) was first reported in our laboratories.[5,6] This binary solvent mixture has proven to be an exceptional medium for conducting a wide range of organic reactions. A large number of cellulose derivatives including esters, ethers, carbamates, and sulfonates have been synthesized. In previous syntheses in our laboratories, cellulose was reacted with a number of acyl chlorides in this solvent utilizing triethylamine (TEA) as an acid acceptor. High yields (90–98%) with DS of 2.4–2.8 were obtained. Controlled acylations were also conducted with acetyl chlorides by varying the stoichiometry of the reagents to produce DS values varying from 0.8 to 2.6.[1] Additionally, the macromolecular aspects of cellulose and its derivatives have been characterized in this solvent system.[7–9]

Samaranayaske and Glasser reported that although acyl chlorides are very reactive most with the exception of acetyl chloride are practically insoluble in LiCl/DMAc in the presence of TEA and that uncontrolled heterogeneous reactions resulted.[2] The authors proposed utilizing acid anhydrides or acids in combination with suitable activators in LiCl/DMAc for homogeneous cellulose acylation at low DS.

Carbodiimides have been successfully used as coupling agents for the synthesis of peptides, nucleotides, and polynucleotides,[10] but they are not generally utilized for the preparation of carboxylates due to the relatively low reactivity. However, acylation of various alcohols has been accomplished using dicyclohexylcarbodiimide (DCC) with a dialkylaminopyridine (DAAP), preferably 4-pyrrolidinopyridine (PP), as a catalyst.[11–15]

To date, only a few reports can be found in the literature regarding unsaturated cellulose ester derivatives.[16–18] Such systems would allow for property modification by postreactions such as bromination, oxidation, or graft polymerization with vinyl monomers. The objective of this research was to find appropriate reaction conditions for controlled acylation of cellulose with various unsaturated carboxylic acids or acid anhydrides in LiCl/DMAc homogeneous solutions with the DCC and DAAP binary catalyst system. Here, we targeted cellulose derivatives possessing pendant alkenyl groups with low DS and solubility in single organic solvents. These cellulose derivatives were studied for graft polymerization with hydrophilic and hydrophobic vinyl monomers in order to prepare stimuli-responsive membranes or interpenetrating networks.

EXPERIMENTAL

Materials

Reagent-grade cellulose used in this study was obtained from J. T. Baker Co. This material is microcrystalline, unfractionated with an $M_w = 1.5 \times 10^5$. Various acids and acid anhydrides, including methacrylic acid and methacrylic anhydride (MAA; MAAn), crotonic acid and crotonic anhydride (CRA; CRAn), vinyl acetic acid (VAA), fumaric acid monoethyl ester (FAME), and cinnamic acid (CINA) and all other reagents were purchased from Aldrich Chemical Co. and used as received, unless specifically noted.

Synthesis

Cellulose Pretreatment

Cellulose was pretreated as follows: Twenty grams of cellulose powder was first slurried in 100 mL methanol (MeOH) overnight and filtered. To the swollen cellulose, another 100 mL MeOH was added, followed by stirring for 1 h and filtering. This procedure was repeated an additional time with MeOH, followed by three similar repetitions with 100 mL of DMAc to complete the solvent-exchange swelling process for facilitating cellulose dissolution. The actual amount of cellulose per gram of swollen material was determined by weighing samples after drying in a vacuum oven at 80°C for 48 h. The average cellulose content for this treated material was about 0.4 g per g of swollen sample.

Cellulose Dissolution

A dry, 250 mL three-necked flask was equipped with a thermometer, a nitrogen inlet, a drying tube, and a mechanical stirrer. The LiCl/DMAc binary solvent mixture was prepared by dissolving 9 g LiCl in 100 mL DMAc at 70–80°C. This LiCl/DMAc solvent mixture was cooled to 40–50°C and 2.0 g cellulose or 0.037 mol of hydroxyl functionality was added followed by stirring until clear.

Cellulose Acylation

The cellulose LiCl/DMAc solution was further cooled to 25°C. Acylation of cellulose was conducted *in situ* by adding the formulated amount of DCC, a tertiary amine catalyst (PP or DMAP), and an unsaturated acid or acid anhydride in sequence. In the case of the VAA acylating agent, distilled VAA was used and the cellulose solution was cooled below 10°C to avoid spontaneous polymerization. The acylation reaction was monitored with FTIR spectroscopy at specific time intervals. Disappearance of the DCC absorbance at 2117 cm^{-1} was regarded as the end of acylation.

Purification of Acylated Cellulose

The acylated cellulose was separated by first precipitating the reaction solution into water to remove LiCl, DMAc, and most of the unreacted acid. The precipitant was then filtered, washed with several aliquots of water, and finally extracted with MeOH in a Soxhlet extractor for 2 days to completely remove hydrated DCC–dicyclohexylurea (DCU) from the acylated cellulose. The extracted cellulose derivative was then dried in a vacuum at 30–35°C for 48 h and weighed to calculate the yield.

Characterization

Spectroscopy

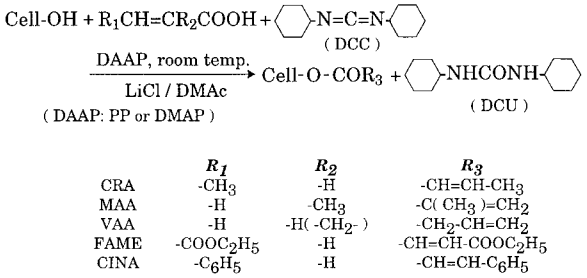
Acylated cellulose film samples were prepared by solution casting with dimethyl sulfoxide (DMSO). FTIR spectra were obtained with a Galaxy 2020 spectrometer (Mattson Instruments Co.). For NMR characterization, samples were dissolved in DMSO-d_6 solvent. ^{1}H-NMR spectra were obtained with a Bruker AC-200 spectrometer.

Elemental Analysis

Elemental analyses on derivatives were performed by M-H-W Laboratories of Phoenix, AZ. Samples were dried in a vacuum oven at 30–35°C for 48 h prior to analysis.

Viscosity Measurements

A Contraves LS-30 rheometer was employed for viscosity measurements at 25°C. The solutions of acylated celluloses were prepared by dissolving a known amount of dry sample in DMSO followed by dilution for testing. Intrinsic viscosities were calculated using the Huggins equation.



	R_1	R_2	R_3
CRA	$-CH_3$	-H	$-CH=CH-CH_3$
MAA	-H	$-CH_3$	$-C(CH_3)=CH_2$
VAA	-H	$-H(-CH_2-)$	$-CH_2-CH=CH_2$
FAME	$-COOC_2H_5$	-H	$-CH=CH-COOC_2H_5$
CINA	$-C_6H_5$	-H	$-CH=CH-C_6H_5$

Scheme 1 Acylation of cellulose with various unsaturated carboxylic acids.

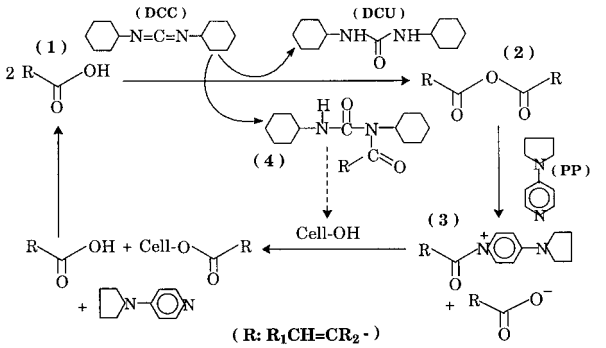
RESULTS AND DISCUSSION

Basic Mechanism of Acylation with DCC/Dialkylaminopyridine

It is well known that acylation of an alcohol with an acyl chloride or a carboxylic anhydride is successful in the presence of an equivalent amount of triethylamine or pyridine. But this generally acceptable approach is not suitable for esterification of heat-sensitive carboxylic acids or acylation of sterically hindered alcohols. It has been shown that these problems can be overcome by the incorporation of DCC and a dialkylaminopyridine (DAAP).[10–14] The utility of this procedure was observed in the preparation of phenyl benzoate from phenol and benzoic acid: (a) In the presence of DAAP alone, the reaction did not proceed; (b) in the presence of DCC alone, the yield of phenyl benzoate was only 10%; and (c) in the presence of both reagents, the reaction could be accomplished at mild conditions with a high yield of 94%.[13]

In this work, the DCC–DAAP binary catalyst system was utilized for the acylation of cellulose with selected unsaturated carboxylic acids or acid anhydrides. The corresponding reaction conditions are illustrated in Scheme 1.

The reaction mechanism for the cellulose acylation with DCC–DAAP is illustrated in Scheme 2 based on previous literature[13,15] and our experimental evidence. The carboxylic acid (**1**) is first converted to the anhydride (**2**) by DCC with formation of DCU. The anhydride then reacts with DAAP to form an activated acyl pyridinium species (**3**). This highly reactive complex is readily



Scheme 2 Mechanism of cellulose acylation with DCC–PP.

esterified with a cellulose hydroxyl group to generate the designated ester and the reusable acid and catalyst for subsequent cycles. Another possible mechanism yielding the cellulose ester is the formation of *N*-acylurea (**4**) from the reaction of DCC and acid. The species may also react with a cellulose hydroxyl group to yield the corresponding ester.

The proposed pathway is partially confirmed in our study of cellulose acylation with CINA and other acids. IR spectra of cellulose derivatized with CINA are illustrated in Figure 1. After acylation begins, the initial C=O stretching of the conjugated aryl carboxylic acid of CINA is observed at 1700 cm^{-1}. Additional absorption bands are observed between 1700 and 1771 cm^{-1} which represent the formation of the acid anhydride (1733 and 1771 cm^{-1} C=O stretching of anhydride) and acid ester (1711 cm^{-1} C=O stretching of ester), respectively.

Other experimental facts also support this mechanism, as illustrated in the reaction of the fumaric acid ester (FAME) with cellulose. In this case, the vinyl group is conjugated with carbonyl functionality; thus, if the carboxyl group reacts with DCC or PP to yield to the corresponding anhydride or acyl pyridinium species, the proton signals should be shifted (Figs. 2–4). These shifts were observed in the ^{1}H-NMR spectra of FAME with DCC and/or PP in DMSO-d_6 solutions (Figs. 3 and 4). Initially, the two protons of the vinyl group in FAME are identical (no splitting) with a signal at 6.69 (Fig. 2). When PP was added to FAME, two pairs of split signals are recorded along with the original proton signal of FAME. These pairs of split signals represent the two protons of the double bond in FAME and two protons on the pyridinium ring (originally at 6.42–6.48) which

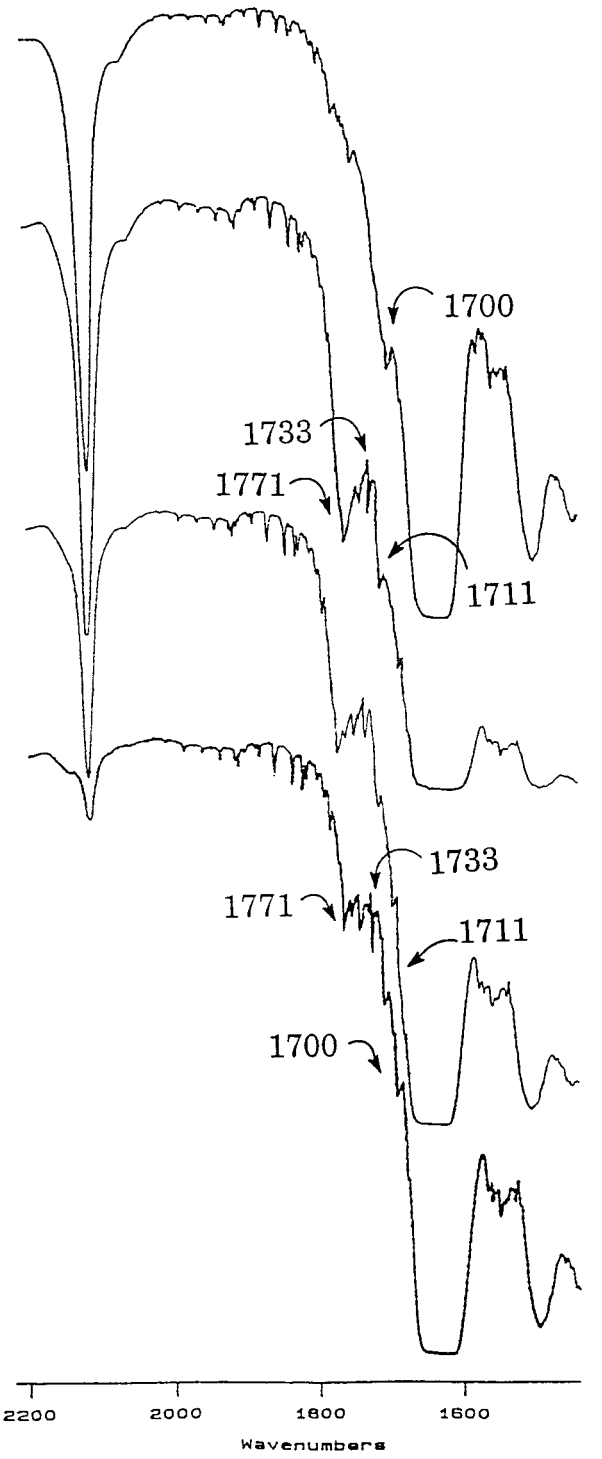


Figure 1 Cellulose acylation with CINA and PP–DCC catalyst system in LiCl/DMAc solution monitored by FTIR (Sample CE-22). From top to bottom: At the beginning of acylation, acylation reaction after 12, 24, and 48 h.

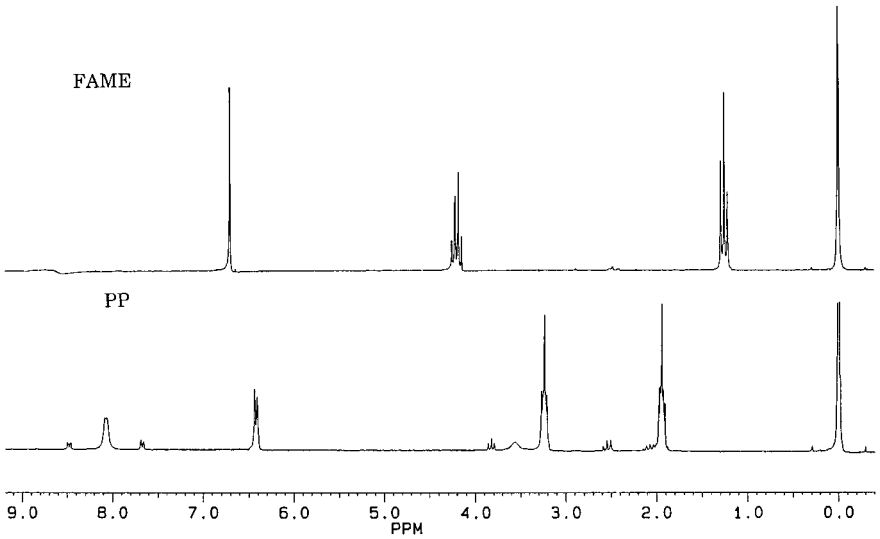


Figure 2 ^{1}H-NMR spectra of FAME and PP (DMSO-d_6).

were shifted and split after the formation of the corresponding complex. After FAME reacts with DCC, two split signals also appear at 6.53–6.61 and 7.01–7.09, representing proton signals of *N*-fumarylurea and FAME anhydride, respectively.

Hassner and co-workers reported that of many pyridine catalyst systems examined only a few of the 4-substituted pyridines investigated behaved as acylation catalysts.[14] The most effective catalysts were found to be 4-pyrrolidino-pyridine (PP) and 1,1,3,3-tetramethyl-4-(4-pyridyl) guanidine ($C_5H_4—N—N=C—[N(CH_3)_2]_2$). Activation of these acylation reactions by the 4-substituted pyridine might be due to the ability of the 4-dialkylamino substituent to donate electrons and thus to stabilize the acyl pyridinium intermediate.

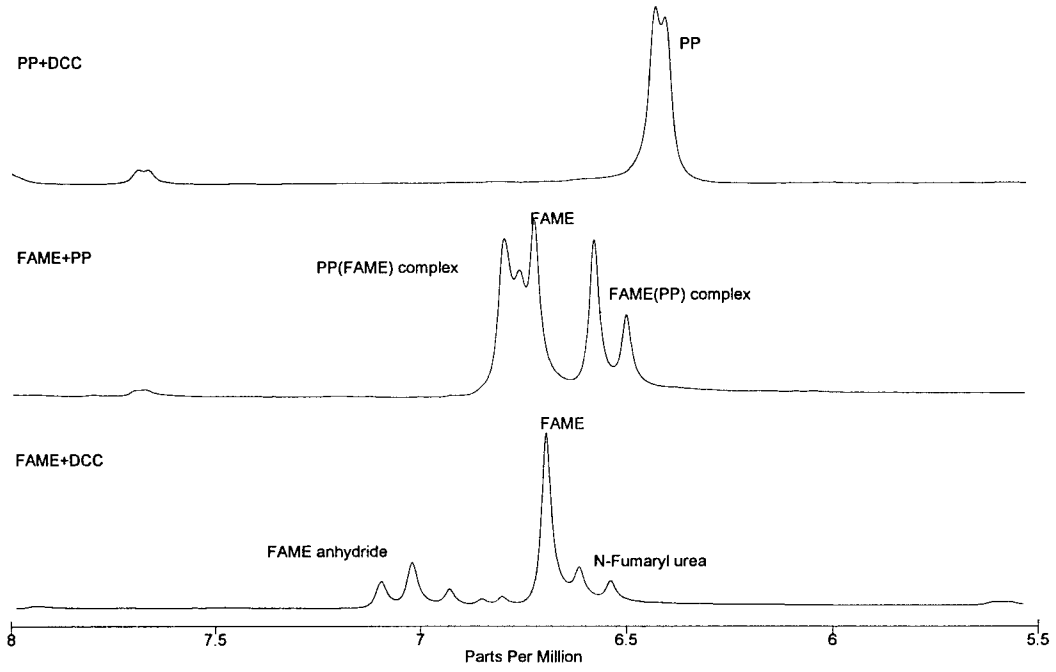


Figure 3 ^{1}H-NMR spectra of FAME alkenyl proton signals after PP or DCC added (DMSO-d_6).

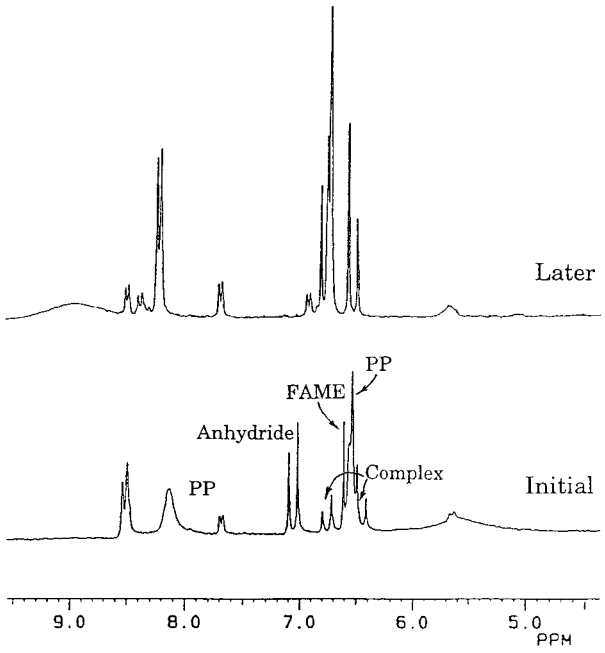


Figure 4 ^{1}H-NMR spectra of FAME with PP and DCC (DMSO-d_6). From bottom to top: just after mixing and 3 h later.

Cellulose Acylation for Selected Unsaturated Carboxylic Acids and Acid Anhydrides

Since cellulose is a linear condensation polymer, consisting of D-anhydroglucoses units joined together by β-1,4-glucosidic bonds, it can be considered as a trihydric alcohol with one primary hydroxyl at the 6-position and two secondary hydroxyl groups at the 2- and 3-positions. According to the basic mechanism of acylation of an alcohol with DCC/DAAP discussed above, a variety of carboxylic acids and acid anhydrides might be used to prepare cellulose ester derivatives. The selected unsaturated carboxylic acids and acid anhydrides reacted with cellulose are shown in Scheme 1. Clearly, the differences in structure and reactivity of acids or acid anhydrides affect the DS in the final products.

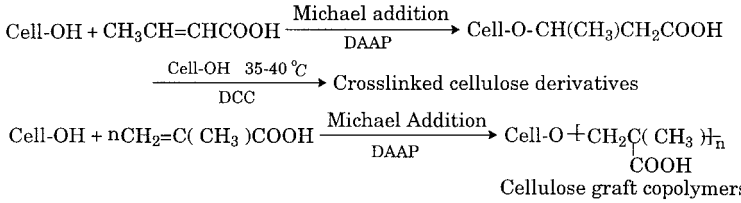
Acylation with CRA (CRAn) and MAA (MAAn)

The reaction conditions and the results of cellulose acylation with crotonic acid (CRA, $CH_3CH{=}CH{-}COOH$) and methacrylic acid [MAA, $CH_2{=}C(CH_3){-}COOH$] and their anhydrides (CRAn and MAAn) are given in Table I. Analysis of the yields of acylation with either the acid or the corresponding acid anhydride (CE-1/CE-3, CE-11/CE-12, CE-2/CE-4) indicates only a slight advantage in using the latter. This is likely due to the twofold increase in the concentration of reactive acyl groups in the anhydride. Although PP has been reported to be more efficient than is DMAP (1.0 vs. 0.63) for the acylation 1,1-diphenylethanol,[14] the efficiency differences in our systems

Table I Results of Cellulose Acylation with CRA (CRAn) and MAA (MAAn)

	Reaction Conditions			
Sample Code	Molar Ratios[a]	Temp (°C), Time (h)	Yield (%)[b]	Solubility[c]
CE-1	CRA (1.0), PP (0.01)	25, 48	24.8	SW
CE-3	CRAn (1.0), PP (0.01)	25, 48	30.2	Sol. in hot DMSO
CE-5	CRAn (1.5), PP (0.015)	25, 48	35.1	Sol. in hot DMSO
CE-11	CRAn (1.5), DMAP (0.05)	25, 48	51.0	SW
CE-12	CRA (1.5), DMAP (0.05)	40, 48[d]	52.7	SW
CE-17	CRAn (1.2), PP (0.05)	35, 16[d]	53.9	SW
CE-2	MAA (1.0), PP (0.01)	25, 48	23.8	SW
CE-4	MAAn (1.0), PP (0.01)	25, 48	26.7	SW
CE-6	MAAn (1.5), PP (0.015)	25, 24 +40, 24	—[e]	Gel sol. in DMSO
CE-7	MAA (1.5), DMAP (0.05)	40, 48	—[e]	Gel sol. in DMSO
CE-19	MAA (1.0), PP (0.05)	25, 63	30.8	SW

[a] Molar ratio of acid or acid anhydride and catalyst to hydroxyl functionality; moles of DCC used was equal to that of acid or acid anhydride.
[b] Yield calculation based on three hydroxyl substitution.
[c] Testing solvent: DMSO; SW: swollen, sol: dissolved.
[d] Gelation occurred during the last stage of reactions.
[e] During extraction with MeOH, products became highly swollen gels.



Scheme 3 Possible side reactions in the cellulose acylation reaction.

(CE12/CE17, CE-5/CE-11) are less evident, probably due to the long reaction times. Additionally, the two carboxylic acids (CRA, MAA) and their anhydrides (CRAn, MAAn) are typically α,β-unsaturated carbonyl systems which reduce reactivity with the alcohol. This is the likely reason for the low yields of CE-1–CE-4 and CE-19.

In attempts to enhance the rate of acylation by increasing the reaction temperature to 35 or 40°C during the preparation of CE-12, CE-17, CE-6, and CE-7, unexpected results were obtained. In the reactions with CRA and CRAn, gelation occurred during the last stage of acylation. DMSO-soluble, gel-like products were also apparent upon extraction with methanol after the reaction with MAA (MAAn). Evidently, side reactions of the hydroxyl group with the conjugated double bond of the acid via a Michael addition and subsequent dehydration to form crosslinked gels or polymerization to MeOH-swollen graft copolymers occur as shown in Scheme 3.[19]

The acylated cellulose derivatives of MAA and CRA or their anhydrides could not be dissolved in DMSO at room temperature. Some samples, however, were soluble at elevated temperature. Therefore, we cannot rule out gel formation from aggregation behavior of linear derivatives.

Acylation with VAA, FAME, and CINA

Three other unsaturated vinyl acids VAA (CH_2=CH—CH_2—COOH), FAME (C_2H_5OOC—CH=CH—COOH), and CINA (C_6H_5—CH=CH—COOH) were utilized as acylating reagents. Although from a structural point of view FAME and CINA are both α,β-unsaturated acids, greater steric effects at the β-position to the alkenyl group appear to decrease the possibility of the Michael addition side reactions observed for the acylation with CRA and MAA. The VAA reagent has no conjugation, so Michael addition should be less favorable. The reaction conditions and yields are listed in Table II.

From the reaction parameters (catalyst concentrations, reaction temperature, and time) for the preparation of CE-21, CE-26, and CE-22 or CE-24, it can be seen that the relative reactivity with cellulose is FAME $\gg$ VAA $>$ CINA. The accelerated acylation in the FAME reactions may be due to formation of a stable intramolecular complex with the acyl pyridinium inter-

Table II Results of Cellulose Acylation with VAA, FAME, and CINA

	Reactions Conditions			
Sample Code	Molar Ratios[a]	Temp (°C), Time (h)	Yield (%)[b]	Solubility[c]
CE-20	VAA (1.1), PP (0.06)	21.5, 42	54.9	sol. in DMSO
CE-26	VAA (1.0), PP (0.04)	25, 28	48.7	sol.
CE-21	FAME (1.1), PP (0.055)	25, 5	43.2	sol.
CE-23	FAME (1.0), PP (0.03)	21, 5	39.2	sol.
CE-22	CINA (1.1), PP (0.05)	25, 48	28.3	sol.[d]
CE-24	CINA (1.0), PP (0.08)	25, 48	33.3	sol.[d]
CE-28	CINA (1.0), PP (0.10)	25, 58	39.4	sol.[d]

[a] Molar ratios of acid or acid anhydride and catalyst to hydroxyl functionality; moles of DCC used was equal to that of acid or acid anhydride.
[b] Yield calculation based on three hydroxyl substitution.
[c] Testing solvent: DMSO; sol: dissolved.
[d] Cell—O—CINA was also dissolved in DMAc.

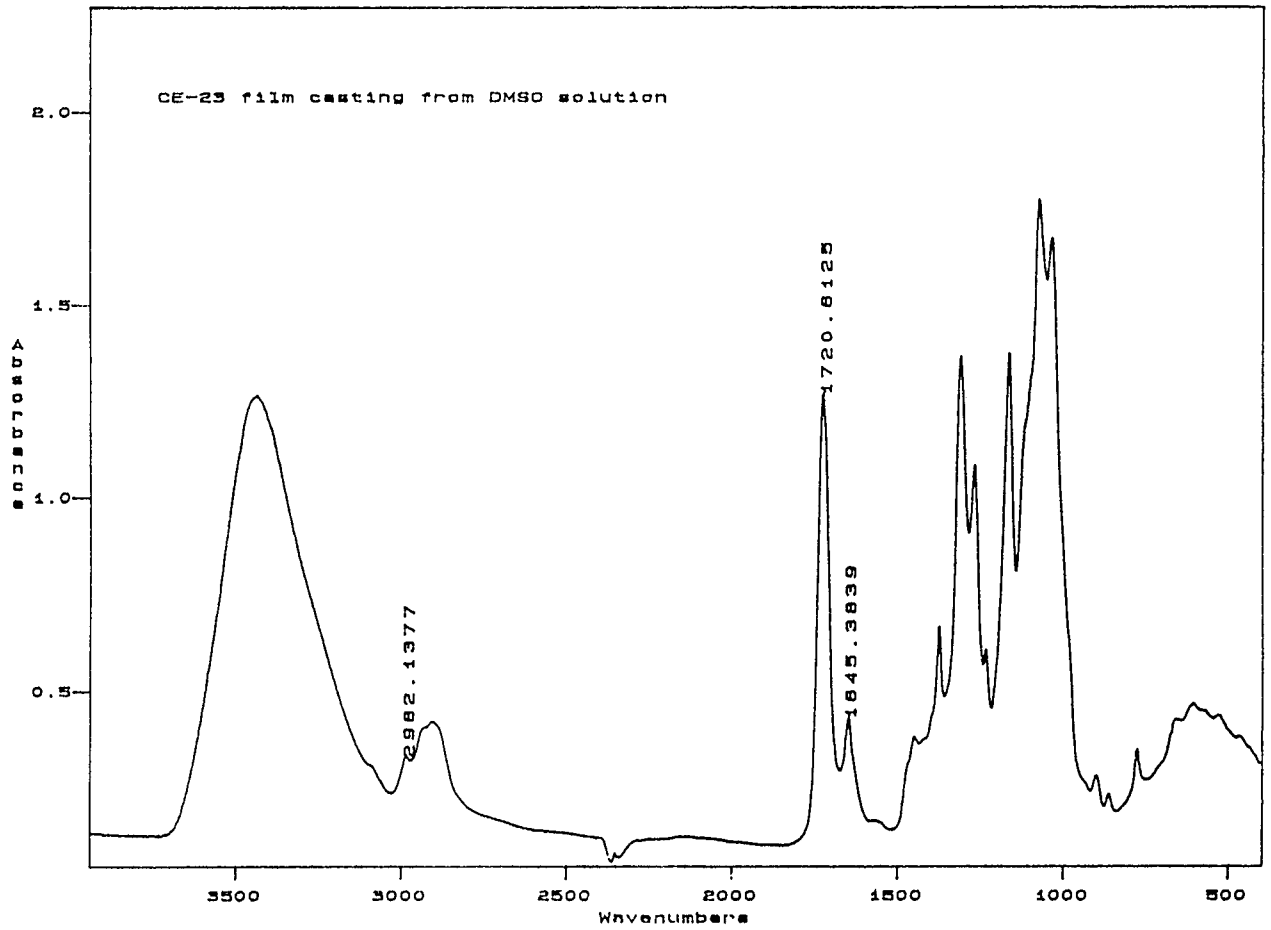


Figure 5 IR spectrum of CE-23 (Cell–O–FAME) film cast from DMSO solution.

mediate. The ^{1}H-NMR spectrum of FAME with DCC and PP in DMSO-d_6 is shown in Figure 4. Initially, the alkenyl proton signals of FAME appear at 6.69 and the four proton signals of the pyridinium ring of PP appear at 6.45–6.54, and 8.02–8.18, respectively (Fig. 2). A series of additional separated signals appear consistent with shifted alkenyl protons resulting from FAME reacting and complexing with DCC and PP (also shown in Fig. 3 as mentioned in the context). After extended acylation time, the alkenyl proton signals of the anhydride disappear at 7.01–7.09.

The acylated cellulose esters of FAME and VAA are soluble in DMSO, if the derivative is not completely dried during the purification procedure. Only the CINA–cellulose derivatives are readily soluble from the completely dried state, probably a result of the disruption of hydrogen bonding by the cinnamyl group even at the lower degrees of acylation (CE-22, CE-24, and CE-28). The intrinsic viscosity of CE-22 and CE-28 samples are 2.52 and 2.80 dL/g, respectively. The solubility of FAME- and VAA-acylated celluloses might be improved by utilizing higher concentrations of the PP catalyst to obtain high DS.

Characterization of Acylated Celluloses

FTIR Spectroscopic Characterization

IR spectra of both DMSO solutions and cast films of the respective cellulose derivatives are shown in Figures 5–7 and summarized in Table III. IR spectra of these unsaturated esters typically exhibit strong ester carbonyl absorption bands at 1710–1735 cm^{-1}. Two additional medium absorption bands are observed around 1635–1645 and 3020–3090 cm^{-1}, respectively, related to C=C stretching and =C—H stretching of the alkenyl group. A very broad, strong absorption band be-

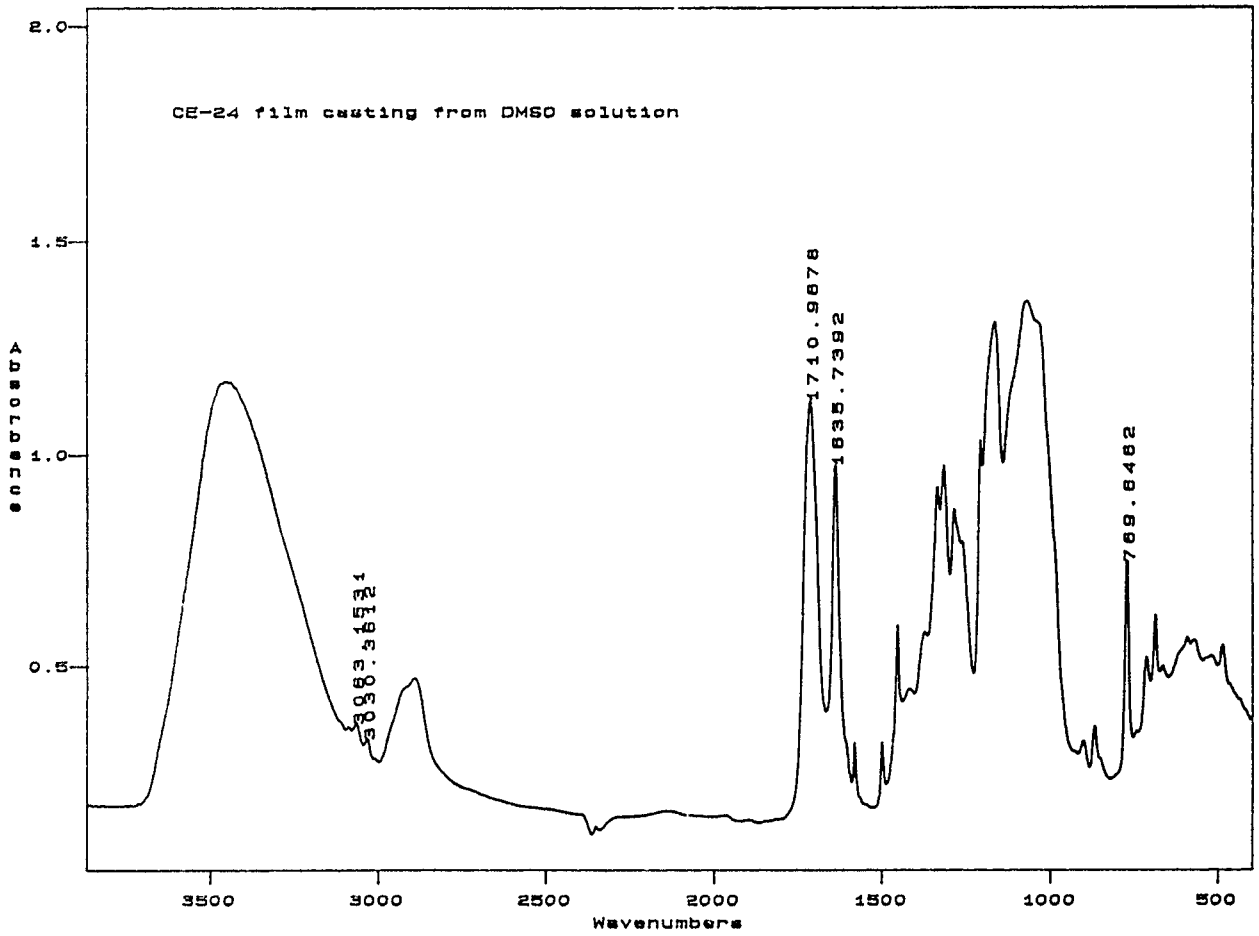


Figure 6 IR spectrum of CE-24 (Cell–O–CINA) film cast from DMSO solution.

tween 3200 and 3650 cm^{-1} represents the O—H stretching of free and bonded hydroxyl groups in the cellulose matrix. Unfortunately, unmodified cellulose is not soluble in DMSO for comparison with the cellulose derivatives.

NMR Spectroscopic Characterization

NMR techniques have been extensively applied to the study of cellulose and its derivatives. Spectral resolution is often poor due to incomplete dissolution and high viscosity of the cellulose solution. Line broadening and overlapping resonance bands add to analysis problems. However, some of these difficulties have been overcome using two-dimensional (2D) COSY NMR techniques.[20–22]

Proton NMR data of unsubstituted and acetylated celluloses from previous literature are listed in Table IV.[20–21] The specific proton signals for hydroxyl groups are 5.2, 5.3, and 5.65, representing OH-3, OH-6, and OH-2, respectively. These chemical shifts of the hydroxyl protons were also observed in our study and confirmed by adding a small amount of trifluoroacetic acid (TFA) to a ^{1}H-NMR sample in DMSO-d_6 to shift both residual water and hydroxyl protons out of the spectral region of interest without perturbing the chemical shift of the anhydroglucose ring protons and the protons of acyl groups. Typical ^{1}H-NMR spectra of CINA- and FAME-acylated cellulose samples in DMSO-d_6 with and without TFA are shown in Figures 8 and 9, respectively.

The signals of protons attached to the carbons on the anhydroglucose ring are not affected by elevating the temperature of the measurement. However, after substitution, larger shifts were observed at the position of the protons attached to the carbon with hydroxyl groups (H-2, H-3, and H-6), but H-1 remained unchanged at 4.65 (Table

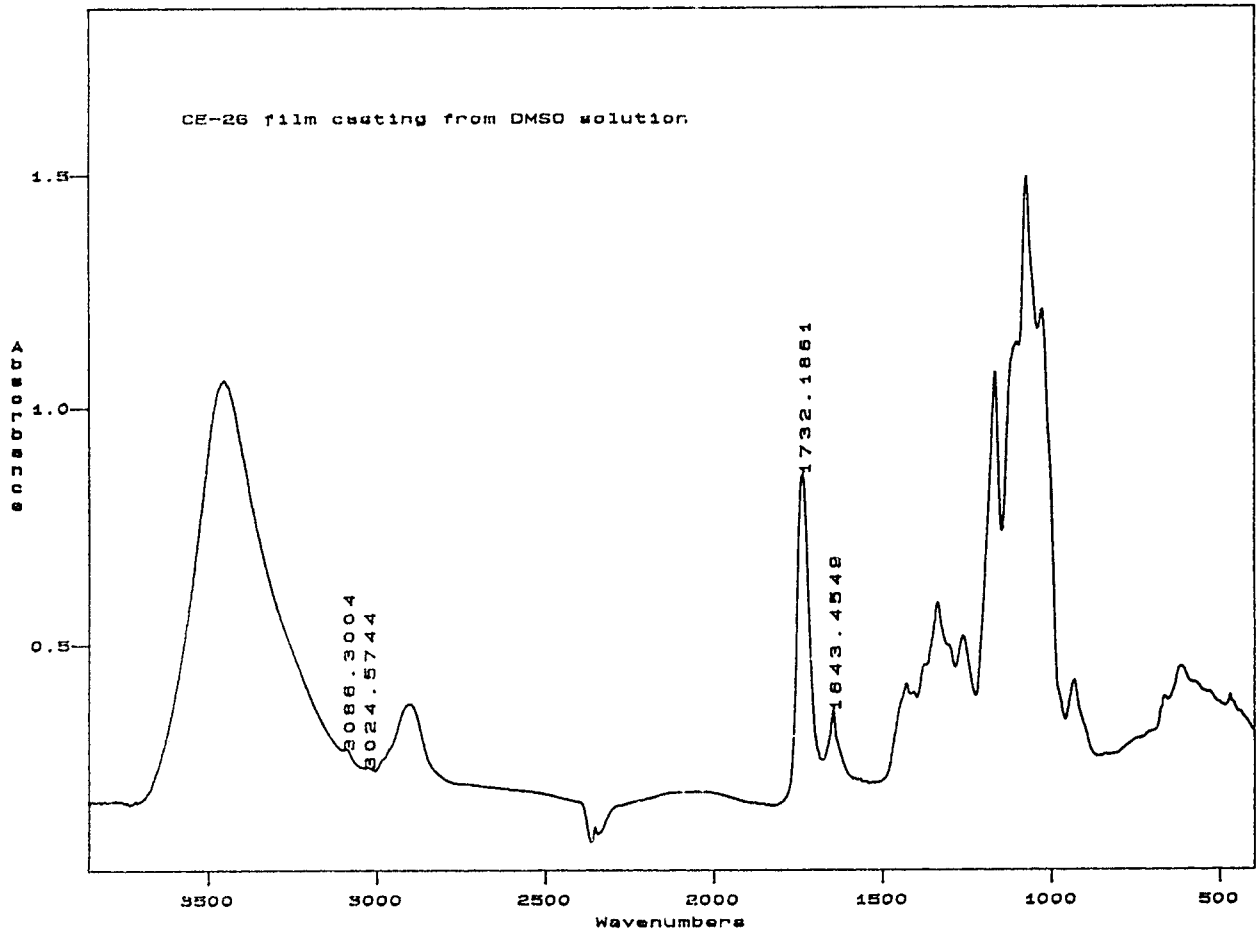


Figure 7 IR spectrum of CE-26 (Cell–O–VAA) film cast from DMSO solution.

IV). The literature data and our NMR data of the unsaturated acids allowed for the assignment of the proton signals of the unsaturated acyl group in the VAA, FAME, and CINA cellulose esters (Table V).

Determination of Degree of Substitution

DS values were calculated from the gravimetric yields and the elemental analyses of the various derivatives. ^{1}H-NMR spectra of FAME and CINA of cellulose derivatives were also used to calculate the DS. The integration data of one of the alkenyl proton signals compared to that of the residual hydroxyl proton signals allowed DS values of cellulose derivatives to be determined. The DS data of these acylated cellulose derivatives are summarized in Table VI. Under the conditions of this work, we were able to obtain DS ranging from 0.25 to 0.55.

Table III Characteristic IR Absorption Bands of Unsaturated Carboxylic Cellulose Esters (cm^{-1})

Group, Vibration	Cell—O—VAA	Cell—O—FAME	Cell—O—CINA
=C—H, stretching, deformation	3024, 3086	2067	3030, 3063
—C=O, stretching	1732	1720	1710
—C=C, stretching	1643	1645	1635
—C—H, aromatic, out-of-plane Deformation (5 adjacent H)	—	—	769

Table IV ^{1}H-NMR Spectra Data of Unsubstituted Cellulose and Triacetate Derivatives

Chemical Shifts δ (ppm)[a]				Chemical Shifts δ (ppm)[b]		
C—H		O—H		C—H (25°C)		C—H (80°C)
H-1	4.65	OH-3	5.2	H-1	4.65	4.65
H-2	3.05	OH-6	5.3	H-2	4.52	4.55
H-3	3.45	OH-2	5.65	H-3	5.06	5.04
H-4	3.4			H-4	3.65	3.68
H-5	3.15–3.2			H-5	3.81	3.77
H-6S	3.6			H-6S	4.22	4.26
H-6R	3.65			H-6R	3.98	4.04

[a] Unsubstituted cellulose in DMAc-d_6/LiCl solution at 70°C; 2D ^{1}H and ^{1}H—^{13}C correlated NMR data adopted from Ref. 20.
[b] Cellulose triacetate in DMSO-d_6; ^{1}H-NMR chemical shift data adopted from Ref. 21.

CONCLUSIONS

The dicyclohexylcarbodiimide (DCC)/4-dialkylaminopyridine (PP or DMAP) binary catalyst system is effective for cellulose acylation with unsaturated carboxylic acids or acid anhydrides near room temperature. The extent of acylation or the degree of substitution (DS) is influenced by the amount of the 4-dialkylaminopyridine catalyst as well as the structural characteristics of the specific acids used. DS values calculated from the different methods were in reasonable agreement and ranged from 0.25 to 0.55.

The extent of acylation is primarily attributed to the reactivity of acids or acid anhydrides. The structural variations in the acids and anhydrides

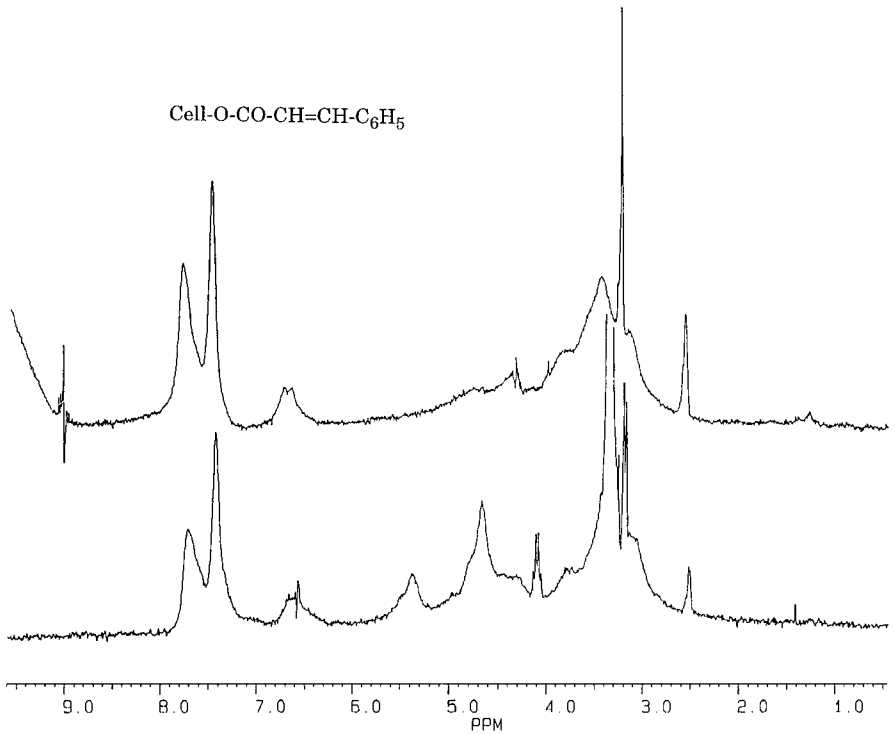


Figure 8 ^{1}H-NMR spectra of CE-22 (Cell–O–CINA) in DMSO-d_6 solution. From bottom to top: the initial spectrum and the spectrum of the sample with TFA.

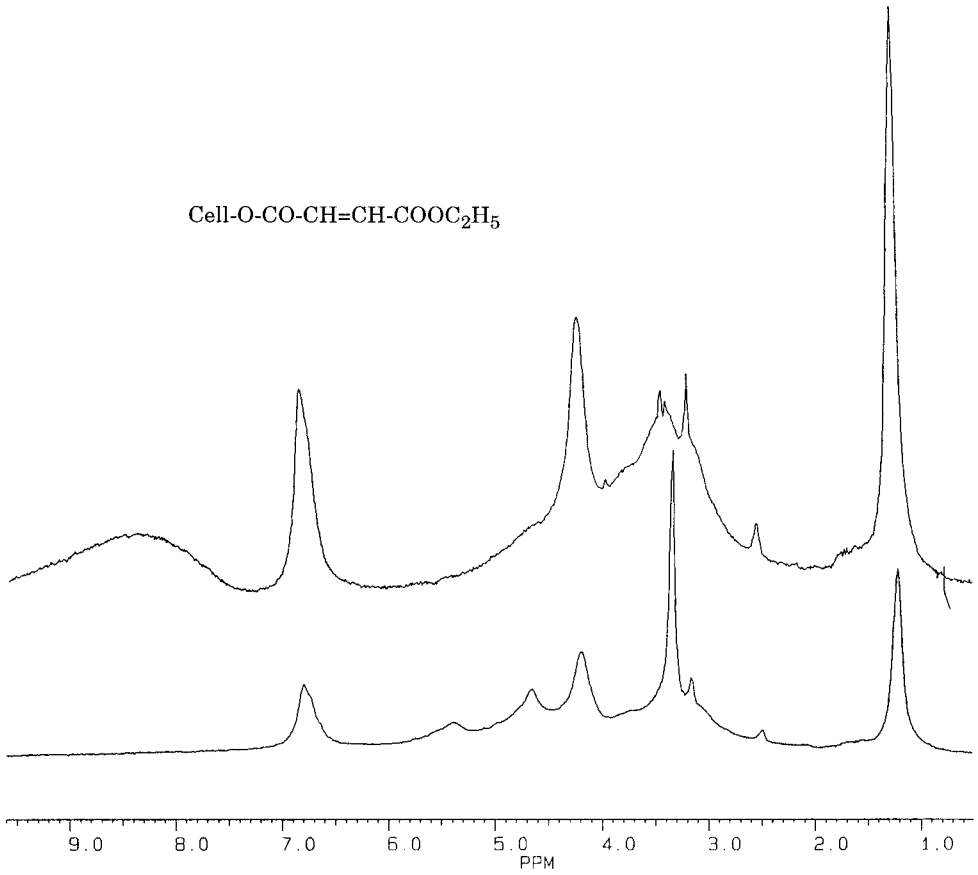


Figure 9 ^{1}H-NMR spectra of CE-23 (Cell–O–FAME) in DMSO-d_6 solution. From bottom to top: the initial spectrum and the spectrum of the sample with TFA.

investigated suggest that conjugation and steric hinderance alter the reactivity. Acylated cellulose derivatives of CRA (CRAn) and MAA (MAAn) are not sufficiently soluble. The acyl groups conjugated with the methylalkenyl group in these acids or acid anhydrides most likely lowered the reactivity of esterification and the extent of reaction. No improvement could be achieved in the CRA

Table V ^{1}H-NMR Spectra Data of Alkenyl Protons of Acylated Celluloses[a]

Chemical Formula	Chemical Shifts δ (ppm)		
	H-1	H-2	H-3
Cell—O—VAA —O—CO—$\underset{1}{CH_2}$—$\underset{2}{CH}$=$\underset{3}{CH_2}$	Overlapped	5.86–5.97	5.14–5.22
Cell—O—FAME —O—CO—$\underset{1}{CH}$=$\underset{1}{CH}$—$COOCH_2CH_3$	6.80–6.82	4.20–4.22	1.25–1.27
Cell—O—CINA —O—CO—$\underset{1}{CH}$=$\underset{2}{CH}$—$\underset{3}{C_6H_5}$	6.56–6.59	7.70–7.74	7.42–7.69

Besides alkenyl proton signals, protons of residual hydroxyl at 5.1–5.9 and protons attached to carbon of anhydroglucose ring at 3.5–5.0 in DMSO-d_6.

Table VI Degree of Substitution (DS) Data (%) Calculated from Different Methods of Determination

Sample Code	DS % from ^{1}H-NMR Spectra	DS % from Yield of Acylation	DS % from Elemental Analysis
CE-20	—[a]	54.9	48
CE-28	36.3	39.2	40
CE-22	25.1	28.3	—
CE-24	29.7	33.3 (63.2[b])	69
CE-28	37.3	39.4 (74.8[b])	72

[a] Alkenyl protons and residual hydroxyl proton signals largely overlapped.
[b] Based on one hydroxyl group substituted.

and MAA reactions by elevating the reaction temperature due to competing side reactions.

Readily soluble derivatives were obtained from cellulose reacted with VAA, FAME, and CINA. FAME was the most reactive species, resulting in rapid acylation and colored products. VAA was also a reactive acid due to the unconjugated carboxyl group, resulting in fairly soluble corresponding cellulose esters with a slight color. The most promising cellulose esters were obtained with CINA. The CINA derivatives were colorless with good solubility in DMSO and DMAc, even at lower DS. The structures of VAA, FAME, and CINA cellulose derivatives were characterized and confirmed with FTIR and NMR spectroscopy. These systems are excellent candidates for further modification or for the synthesis of graft copolymers utilizing the pendant alkenyl groups.

Support for portions of this research from the Office of Navy Research, Gillette Research Institute, and Nalco Corp. is gratefully acknowledged.

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